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Evidence for Nascent Equilibrium Nuclei as Progenitors of Anomalous Transformation Kinetics in a Pu-Ga Alloy

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By alloying Pu with Ga, the face-centered-cubic δ phase can be retained down to room temperature in a metastable configuration, which ultimately yields to chemical driving forces by undergoing the $\delta \rightarrow \alpha'$ isothermal martensitic transformation below $M_s \approx -100$ °C. This transformation is found to exhibit anomalous transformation kinetics, the nature of which has remained elusive for over 30 years. Recently, a “conditioning” treatment—an isothermal hold above M_s —has been shown to dramatically affect the amount of α' phase formed during the transformation. Herein, we report evidence that the conditioning treatment induces the lower-C of the double-C curve, and we furthermore implicate the classical nucleation of equilibrium phases within the conditioning range as the underlying mechanism behind conditioning in Pu-Ga alloys. This mechanism should not be rigorously exclusive to plutonium alloys as it arises from the proximity between the retained metastable phase and the low-energy equilibrium phases.

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Alloying plutonium with gallium yields a complex equilibrium Pu-Ga phase diagram, reflective of the multiple, nearly degenerate phases of the pure element [1–5]. The rich phase diagram of Pu-Ga is no doubt dominated by the effects of f -electron correlation [6–11], and the differences between the properties of ground state α -Pu and δ -Pu serve as prime examples of how these strong correlations can induce dramatically different macroscopic properties including crystal symmetry, ductility, Sommerfeld coefficient, magnetic susceptibility, thermal expansion, etc [3, 12, 13]. As yet, a complete picture does not exist regarding the fundamental factors that ultimately drive plutonium between the α and δ phases. In fact, the sources of entropy responsible for stabilizing δ -Pu in favor of α -Pu are currently unaccounted for [14]. Understanding the α and δ phases of plutonium as well as transitions between them are important components to our appreciation of the role that f -electron correlation plays in engendering the phase stability and physical properties of actinide metals, alloys, and compounds.

The lean gallium (Ga content ≤ 10 at.%) portion of the equilibrium Pu-Ga phase diagram displays no fewer than 13 solid state phase fields as shown in Figure 1(a); but, of these phase fields, only three are single-phase where Ga exhibits appreciable solubility: the face-centered-cubic δ phase, the body-centered-tetragonal δ' phase, and the body-centered-cubic ϵ phase. The balance of the phase fields exist as mixed phase regions consisting of combinations of Ga-miscible, Ga-immiscible, and ordered phases [15, 16]. While increased Ga content tends to stabilize the δ phase toward lower temperatures, it is the slow Ga diffusion within the δ phase that likely permits it to be retained in a metastable state down to room temperature or below (Figure 1(a)), well within several of the mixed phase fields [3–5, 17]. In addition to the limited Ga diffusion in the δ phase, self-irradiation effects from the

alpha-decay of Pu atoms also prohibit true equilibrium by altering chemical composition and lattice periodicity through the accumulation of daughter products, helium bubbles, and defects [18–21].

The metastable δ phase of the Pu-Ga system can be unstable toward transformation to the metastable α' martensite, which occurs at sub-ambient temperatures for Ga concentrations between about 0.6 and 2.5 at.% [16, 22, 23]. The α' product phase forms with the same structure as α -Pu, but the diffusionless character of the transformation traps Ga solute and expands the lattice [22, 23]. This $\delta \rightarrow \alpha'$ transformation is incomplete, resulting in only about 25% α' product by volume due to the strains associated with the large unit cell volume discrepancy between the parent and product phases. For the case of a Pu-1.9 at.% Ga alloy, the $\delta \rightarrow \alpha'$ transformation yields the α' martensitic phase isothermally (*i.e.*, a temperature-dependent incubation time is required) with peculiar double-C kinetics when plotted on a time-temperature-transformation (TTT) diagram (see Figure 1(b)), for which two temperatures define minimum times for the initiation of transformation [24, 25]. While double-C kinetics have been observed and explained in other systems [26, 27], the nature of the double-C in Pu-Ga alloys has defied explanation for over three decades and remains a perplexing component of plutonium science. Understanding the kinetics and mechanisms of the $\delta \rightarrow \alpha'$ martensite in Pu-Ga have profound implications on our appreciation of phase stability in actinides and of martensitic transformations in general.

Recent research has shown that a “conditioning” treatment—which entails an isothermal hold of order hours below a 375 °C anneal, but above M_s —enhances the amount of transformation occurring at low temperature [28]. This conditioning effect seems contrary to con-

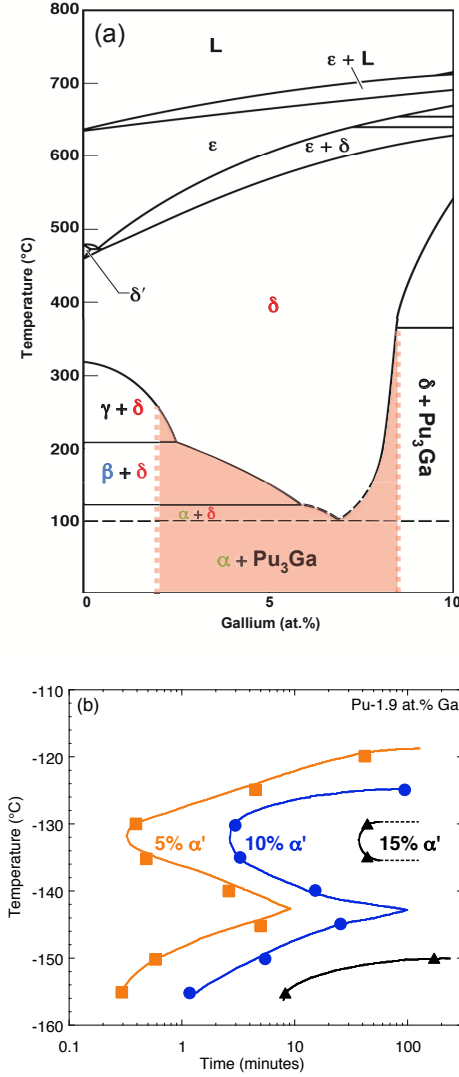


FIG. 1: Phase diagram of the Pu-Ga system and the TTT diagram of Pu-1.9 at.% Ga. (a) The low-Ga portion of the phase diagram of the Pu-Ga system shows the multiple stable equilibrium phases [23]. The red, shaded area bounded by vertical dashed lines represents the region of the phase diagram where the metastable δ phase likely persists due to slow Ga diffusion. (b) The TTT diagram of a Pu-1.9 at.% Ga alloy shows anomalous double-C behavior where the $\delta \rightarrow \alpha'$ transformation occurs in a minimum amount of time at two distinct temperatures [24].

ventional metallurgical precepts, where sub-anneal temperatures should represent vanishingly small perturbations to the system. While these results certainly engender questions surrounding the essential characteristics of conditioning, they also reveal an opportunity to probe the double-C in Pu-Ga alloys by studying the nature of this conditioning treatment and its role in the $\delta \rightarrow \alpha'$ transformation. Here we report results of the impact of conditioning on the $\delta \rightarrow \alpha'$ transformation as

well as a detailed study designed to illuminate the nature of conditioning. We invoke a nucleation mechanism to explain the observed temperature dependencies and transformation-promoting effects of conditioning.

The dramatic effects of conditioning on the $\delta \rightarrow \alpha'$ transformation are highlighted in the composite optical metallography images of Figures 2a and b. Embedded in the δ matrix (background of the image) are acicular features that correspond to the α' product phase. The upper-right triangular portion of each subfigure represents a sample that has been conditioned, while the lower-left triangular portion represents an unconditioned sample. Figure 2a corresponds to a sample that was quenched to -120°C and held for 4 hours (upper-C of the TTT diagram), while Figure 2b represents a sample that was quenched to -155°C and held for 4 hours (lower-C of the TTT diagram). In the upper-C, conditioning enhances the amount of transformation that occurs upon cooling, as indicated by the increase in the size and number of α' particles. However, the overall morphology of the transformation in the upper-C is substantially equivalent irrespective of conditioning, suggesting that conditioning only affects the amount of transformation and not the martensitic mechanism. The conditioning dependence in the lower-C is markedly different from that of the upper-C: without conditioning, no transformation is visible [29]; with conditioning, a large amount of transformation is evident. This observation suggests that conditioning actually enables transformation in the lower-C, and that, without conditioning, only the mechanism responsible for the upper-C is involved in the $\delta \rightarrow \alpha'$ transformation [30].

DSC measurements corroborate the conditioning dependence illuminated in Figures 2a and b. Figure 2c shows DSC traces, heat flow per gram versus temperature, of the $\delta \rightarrow \alpha'$ transformation as a function of cooling. When the sample is not conditioned, a single broad feature is observed in the DSC trace. With conditioning, however, a DSC trace reveals a new peak at lower temperature. Because optical metallography indicates that *only* the upper-C exists without conditioning, then the unconditioned DSC trace can be assumed to be a result of transformation in the upper-C and then scaled by a constant to estimate the contribution of the upper-C with conditioning. This scaling is consistent with the increase in transformation with conditioning observed in Figure 2a. The difference between the raw DSC data with conditioning and the estimate for the conditioning-induced contribution to the DSC trace from the upper-C provides an estimate for the contribution from the lower-C. The new, conditioning-induced peak in the DSC appears to affect the amount of transformation only below -130°C .

These results indicate that conditioning has a very profound effect on the kinetics of the $\delta \rightarrow \alpha'$ transformation, but the results do not provide detailed insight into the mechanism of the conditioning effect. Thus, additional

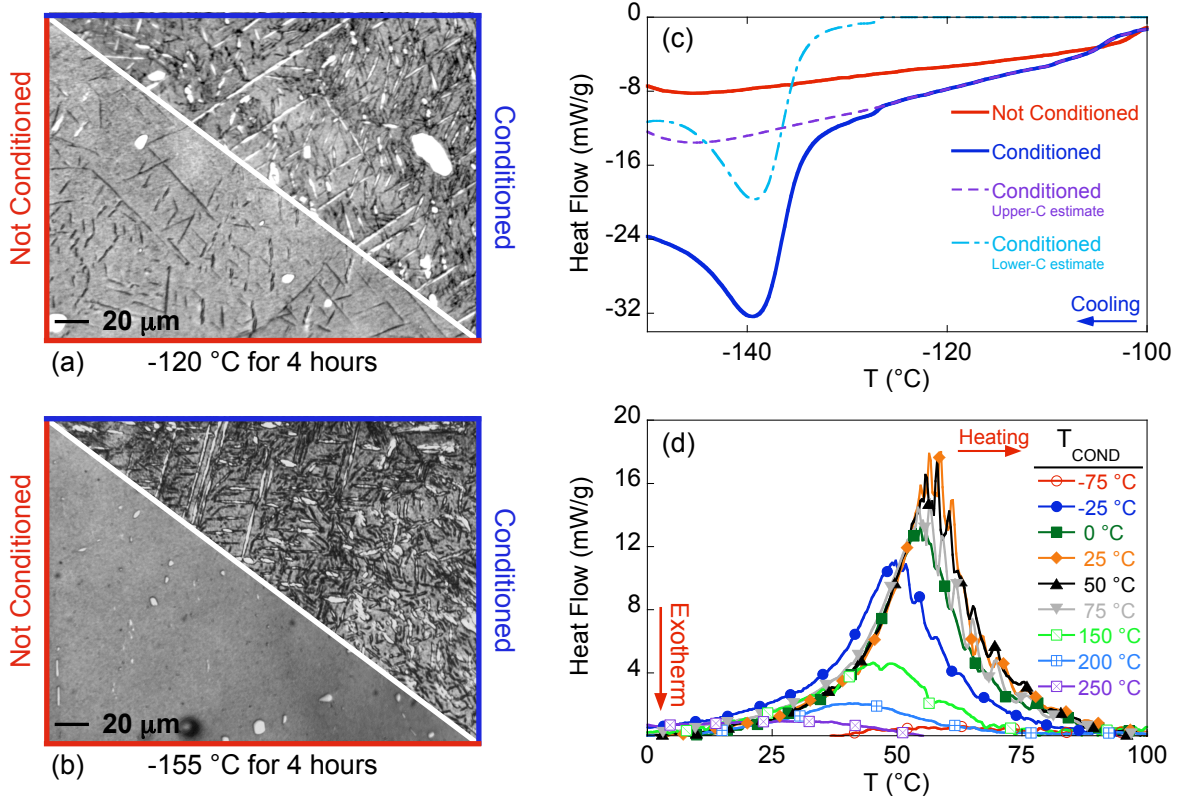


FIG. 2: Phase transformation in Pu-1.9 at.% Ga as revealed by optical metallography and differential scanning calorimetry. Optical micrographs after a 4-hour isothermal hold at -120 °C (a) and -155 °C (b) with (upper-right triangle) and without (lower-left triangle) a previous 8-hour conditioning treatment at room temperature. The high aspect ratio features are the α' product phase embedded in the surrounding δ matrix. Conditioning can be seen to increase the amount of transformation at both temperatures, but it enables the transformation at -155 °C, suggesting that conditioning is responsible for the appearance of the lower-C. (c) DSC traces (heat flow versus temperature) of the $\delta \rightarrow \alpha'$ transformation on cooling with and without conditioning. The upper- and lower-C components of the conditioned curve are estimated from the curve without conditioning (see text). (d) DSC traces showing the $\alpha' \rightarrow \delta$ reversion for various 8-hour isothermal conditioning treatments at T_{COND} .

DSC measurements were undertaken to determine the temperature dependence of conditioning to illuminate the nature of the conditioning effect. Figure 2d shows DSC traces of the $\alpha' \rightarrow \delta$ reversion for 8-hour isothermal holds at various conditioning temperatures T_{COND} . The areas under the reversion peaks in Figure 2d are proportional to the volumetric amount of α' product phase formed during the transformation. Figure 2d reveals that the conditioning effect in Pu-1.9 at.% Ga has a significant temperature dependence. The reversion peak has a maximum area between 25 and 50 °C, but temperatures of -75 and 250 °C produce very little, if any, transformation-promoting effects. Any description of the conditioning effect must explain the increase in the amount $\delta \rightarrow \alpha'$ transformation observed in the micrographs and the DSC traces, but that description must also encompass the temperature dependence of conditioning embodied in Figure 2d.

The complexities of the Pu-Ga phase diagram [Fig. 1(a)] are driven by the presence of nearly degenerate phases. Hypothetical, schematic free energies as a function of Ga content for the δ , β , and α phases are shown as red, blue, and green lines in Figure 3. The red diamond represents the free energy of the δ phase Pu-1.9 at.% Ga alloy used in this study. In (a), the β phase free energy for pure Pu is below that of δ , and it is then energetically favorable for the metastable δ phase of the alloy to decompose into $\beta + \delta$. The free energy gained from this decomposition is represented by the blue circle residing on the tie line connecting pure β -Pu with the Ga-containing δ phase. Reducing the temperature, as in (b), lowers the free energy for $\delta \rightarrow \beta + \delta$, but also permits the $\delta \rightarrow \alpha + \delta$ decomposition, which results in a larger free energy reduction represented by the green square. Reducing the temperature still further, as in (c), results in yet another decomposition path, $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$, with

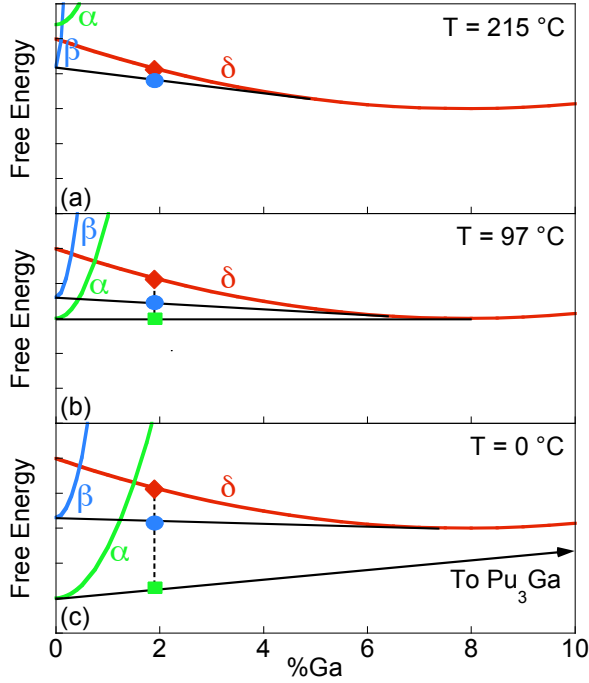


FIG. 3: Schematic free energy-composition diagrams at various temperatures for the δ , β , and α phases of Pu-Ga as a function of Ga content. The decomposition, defined from the black tie lines, of the δ phase of the Pu-1.9 at.% Ga used in this study (red diamond) can lower the free energy of the system; these lower free energies are represented in (a), (b), and (c) by the blue circles, which correspond to the reduction in free energy in creating the β phase, and green squares, which correspond to the reduction in free energy in creating the α phase.

an even greater reduction in free energy.

While there is a chemical driving force for phase transformations into mixed phase microstructures, these transformations are not observed due to extremely slow Ga diffusion, stresses, or strains [3–5, 17]. However, for a Pu-1.9 at.% Ga alloy, nuclei of the pure plutonium phases could form within the metastable δ phase via local distortions of the Pu lattice without diffusion of Ga [31]. The formation of Pu_3Ga nuclei is unlikely, as it would require significant Ga diffusion for a lean 1.9 at.% Ga alloy. Therefore, maintaining a sample of Pu-1.9 at.% Ga at a temperature within one of the mixed phase regions for an extended time could promote the formation of small nuclei of the equilibrium phases of pure Pu. These equilibrium nuclei are referred to as nascent, because they would serve as the roots of a complete transformation given enough time (potentially thousands of years) for their evolution.

Once these postulated nascent equilibrium nuclei (NEN) form, they would be stable with respect to low-temperature excursions. As such, the presence of NEN

would potentially have two transformation-promoting consequences for the $\delta \rightarrow \alpha'$ transformation: (1) increasing the number of available nucleation sites for the α' phase, and (2) serving as progenitor nuclei for the growth of the α' phase. In the first scenario, NEN represent local deviations from the δ phase symmetry, similar to point defects, that could act as nucleation sites for the α' phase. By effectively increasing the number of available nucleation sites for the $\delta \rightarrow \alpha'$ transformation, the development of NEN would increase the amount of transformation through the formation of more α' particles or a reduction of the activation barrier necessary to nucleate the α' phase. This increased amount of transformation product is observed at -120 °C, where the amount of transformation yielded through conditioning is enhanced over that of an unconditioned sample [Figs. 2(a) and (c)]. If the progenitor nuclei are developed at temperatures above the transformation, as in the second scenario above, then the $\delta \rightarrow \alpha'$ transformation may proceed through growth alone, bypassing low-temperature nucleation. This behavior could allow the transformation to proceed at lower temperatures where there is insufficient thermal activation to nucleate the martensite. This scenario is reflected in the data at -155 °C [Figs. 2(b) and (c)], where transformation at a low temperature is induced by conditioning.

While the development of NEN provides a qualitative description for the observed behavior in the optical metallography and DSC studies of the $\delta \rightarrow \alpha'$ transformation with and without conditioning, the presence of these nuclei should be manifested in the behavior of the conditioning effect. Evidence for the existence of these NEN can be inferred through the temperature dependence of the conditioning effect and through the suppression of the conditioning effect with high-temperature treatments, where the NEN should be unstable due to increased atomic migration encouraging the dissolution of the nuclei into the higher-temperature equilibrium phases. Because the positive effects of conditioning occur in a matter of hours—saturating after about 8 hours—we focus here on the formation and decay of α - and β -phase nuclei, and ignore the formation of Pu_3Ga as well as the γ phase, which likely has only a small driving force from the δ phase for a Pu-1.9 at.% Ga alloy.

Classical heterogeneous nucleation can be described by

$$\dot{\mathcal{N}} = \left(\omega_0 e^{\frac{-\Delta G_M}{RT}} \right) \left(n_0 e^{\frac{-\Delta G_c}{RT}} \right), \quad (1)$$

where $\dot{\mathcal{N}}$ is the rate of nucleation, ω_0 is a phonon frequency, ΔG_M is an activation barrier for thermal motion, n_0 is the total number of nucleation sites in the sample, ΔG_c is the free energy required to create a nucleus, R is the gas constant, and T is the temperature. In Equation 1, the leftmost parenthetical term describes the rate at which atoms migrate in and out of a developing

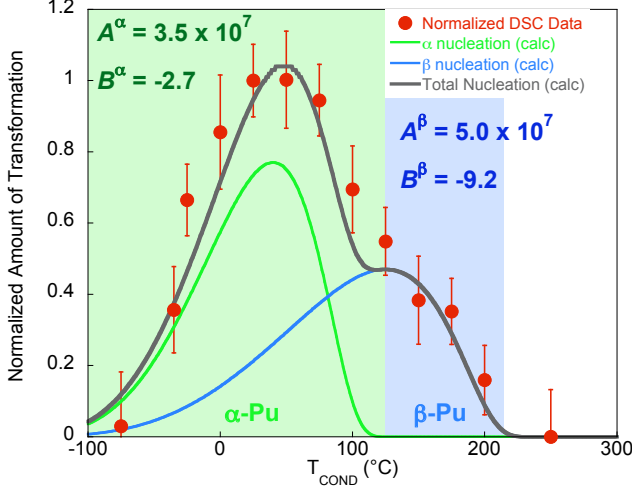


FIG. 4: Evidence for the formation of nascent equilibrium nuclei (NEN). The normalized amount of transformation as a function of T_{COND} (red circles) is determined by integrating the traces of Figure 2d. The green and blue shaded regions represent, respectively, the temperature ranges where the α and β phases of pure plutonium are the most energetically favorable. The solid lines are fits to a classical nucleation equation describing nucleation of the equilibrium α (green line) and β (blue line) phases and their sum (dark gray line).

nucleus, while the rightmost term describes the energy to create a nucleus where ΔG_c includes the driving and inhibiting forces for heterogeneous nucleation:

$$\Delta G_c = \frac{16\pi}{3} \frac{\tilde{S}\gamma^3}{(\Delta G_V + \Delta G_S)^2}, \quad (2)$$

where γ , ΔG_V , and ΔG_S are the surface energy, volume free energy, and strain energy, respectively, associated with the phase transformation, while \tilde{S} is a shape factor for heterogeneous nucleation. The temperature dependence for ΔG_V can be estimated as:

$$\Delta G_V = (T_0 - T) \Delta S, \quad (3)$$

where T_0 is the temperature at which the free energies of the two phases in question are equal and $\Delta S = \Delta H/T_0$ is the entropy of formation (with ΔH as the heat of transformation). Note that ΔG_V , the driving force, is defined as positive for temperatures below T_0 .

If we let $A \equiv 16\pi\tilde{S}\gamma^3/3\Delta S^2$ and $B \equiv \Delta G_S/\Delta S$, then Equation 1 can be recast as:

$$\frac{\dot{N}}{\omega_0 n_0} = \exp \left\{ \frac{-1}{RT} \left[\Delta G_M + \frac{A}{(T_0 - T + B)^2} \right] \right\}, \quad (4)$$

where the temperature dependence of nucleation as a function of three parameters A , B , and ΔG_M is encompassed in the right side of the above equation.

The left side of Equation 4 describes the temperature-independent magnitude scaling of the nucleation rate.

The areas under the curves of the DSC data from Figure 2d are obtained by numerical integration, and correspond to the measured heat of transformation, which is proportional to the volumetric amount of transformation that occurs on cooling. Because the heat of transformation for the $\alpha' \rightarrow \delta$ reversion is not precisely known, the amount of transformation cannot be accurately quantified. Thus, the amount of transformation as a function of conditioning temperature has been normalized to its maximum value, presented in Figure 4 as red circles. The error bars are derived from instrumental noise.

Comparing the normalized amount of transformation as a function of different conditioning temperatures with equal isothermal hold time reveals the temperature dependence of conditioning and its similarities to classical nucleation. The temperature dependence of the experimental data of Figure 4 are fit with two cases of Equation 4: one case each for the nucleation of the α and β phases. The values of T_0 (*i.e.*, the temperatures where $\Delta G^\delta = \Delta G^\beta$ and $\Delta G^\delta = \Delta G^\alpha$) are taken from Turchi *et al.* [32], while the value of $\Delta G_M = 12$ kJ/mol is determined to be the best value for both α and β nucleation. The values of A , in units of J-K²/mol, and B , in units of K, determined from the fits are given in Figure 4 for both nucleation processes. The temperature dependence of the nucleation of the α phase is represented by a green line, while that of the β phase is represented by a blue line. The sum of the two nucleation processes is represented by a dark gray line, which overlaps the data points well.

Deviations from the experimental data are evident on the low-T sides of the individual α and β nucleation curves. These deviations are likely a consequence of Equation 3, which assumes a linear temperature dependence for ΔG_V . This linear temperature dependence is probably valid near T_0 ; but, at temperatures significantly below T_0 , ΔG_V may deviate from that assumption, resulting in discrepancy with the DSC data. It should be noted that the effects of self-irradiation on nucleation are not well understood, and no component of self-irradiation (*e.g.*, radiation-enhanced diffusion) has been included in the description of the DSC data. The fits nonetheless provide compelling evidence, through the temperature dependence of the conditioning effect, that conditioning in Pu-1.9 at.% Ga is a result of the nucleation of equilibrium phases.

In addition to the temperature dependence of nucleation, evidence for the development of NEN through conditioning is observed through the destruction of the positive effects of conditioning with high-temperature treatments. NEN, once formed, should be stable with respect to low temperature excursions, but they should dissolve back into the parent phase when subjected to high temperatures. An annealed and room-temperature-

conditioned Pu-Ga sample was subjected to three post-conditioning treatments (*i.e.*, isothermal holds for varying times immediately following the conditioning treatment), and then thermally cycled through the $\delta \rightarrow \alpha'$ transformation and $\alpha' \rightarrow \delta$ reversion. As before, the measured heat was calculated from the reversion.

Figure 5 shows the results of post-conditioning treatments at three key temperatures: (a) 325 °C, within the stable δ phase field; (b) 225 °C, within the $\beta + \delta$ phase field, where β nuclei can form; and (c) -75 °C, within the $\alpha + \text{Pu}_3\text{Ga}$ phase field. The data have been fit with a simple exponential decay [33] equation to quantify the destruction of conditioning; the “half-life” of the NEN for each post-conditioning temperature is given as $t_{1/2}$. Post-conditioning at 325 °C shows a rapid suppression of the measured heat of reversion, with $t_{1/2}=6$ minutes. Similarly, post-conditioning at 225 °C shows a rapid decrease in the measured heat, with $t_{1/2}=10$ minutes. However, unlike post-conditioning in the δ phase field, post-conditioning in the $\beta + \delta$ phase field still permits a small amount of nucleation of the β phase, accounting for the observed measured heat of reversion near 100 mJ/g that persists for longer holds. Finally, post-conditioning at -75 °C yields, at most, a very slow decay of the measured heat of reversion ($t_{1/2}=32$ hours). While the α -like NEN formed near room-temperature should be stable at sub-ambient temperatures, damage cascades from the nuclear decay of Pu would likely contribute to the destruction of the nuclei. If a radiation damage cascade disrupts a NEN, then that nucleus cannot easily reform at low temperature. The decay of the measured heat with different post-conditioning temperatures behaves as expected for a conditioning treatment described by the formation of NEN.

From the results of our combined metallography and calorimetry study, we conclude that the conditioning effect in Pu-Ga is consistent with the development of nascent equilibrium nuclei. Furthermore, we propose that the development of these nuclei is a new route to affecting a martensitic transformation. In the case of Pu-1.9 at.% Ga, these NEN appear to be responsible for the double-C kinetics observed in the $\delta \rightarrow \alpha'$ transformation, with the nuclei serving as additional nucleation sites in the upper-C while serving as progenitor nuclei for transformation in the lower-C. This mechanism ultimately arises due to a delicate balance between diffusion-limited decomposition, which permits the retention of a metastable phase, and the close proximity of the metastable and energetically preferred equilibrium phases within the free energy landscape. The Pu-Ga system is a prime example of these two criteria, but there is no strict rule within the above formalism that would exclude other systems from exhibiting a similar conditioning effect with dramatic implications for a displacive phase transformation.

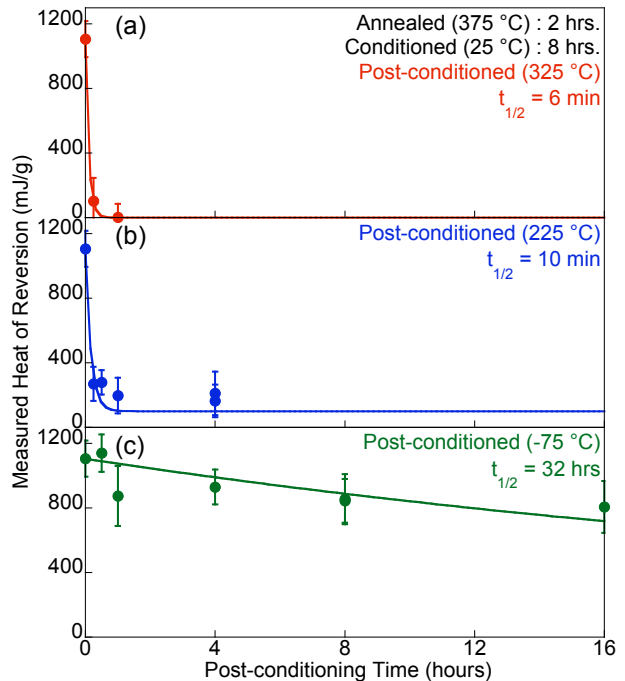


FIG. 5: The decay of α -like NEN as a function of time at three key temperatures. (a) 325 °C, above the temperature range where conditioning occurs; (b) 225 °C, where small effects of conditioning attributed to β nuclei should occur; and (c) -75 °C, where only small amounts of α nuclei are expected to form. Solid lines are fits to a simple exponential decay equation used to extract the half-life, $t_{1/2}$, for each post-conditioning temperature.

METHODS

The optical metallography experiments have been described previously [30], and a sample of the same chemical composition was used in the differential scanning calorimetry (DSC) experiments. Polycrystalline samples of Pu-1.9 at.% Ga were machined into ~ 3 mm diameter discs with a mass of 177 mg and loaded into Au-plated stainless steel pans. To ensure a single phase specimen with a homogeneous Ga distribution, the sample was annealed for 534 hours at 460 °C.

Differential scanning calorimetry data was acquired in a commercial, power compensating Perkin-Elmer Pyris Diamond differential scanning calorimeter previously calibrated with adamantane, indium, and zinc. Preceding each individual experiment, the sample was annealed at 375 °C in the DSC to revert any previous α' product to the δ phase and to eliminate defects and strains accumulated from prior martensitic transformation [34]. Continuous cooling DSC traces were obtained at 20 °C/min. A smooth baseline was subtracted from the data to yield the portion of the DSC trace associated with the transformation of the sample.

The maximum temperatures (T_{max}) for the nucleation of the α and β phases were fairly easily identified from the DSC data. By setting the derivative of Equation 4 to zero at T_{max} , the fits of Equation 4 to the data were reduced to a function of two free parameters: ΔG_M and A . The value of B was then calculated by solving a cubic equation that was a function of the experimentally observed T_{max} as well as the fit parameters ΔG_M and A .

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AUTHOR CONTRIBUTIONS

JRJ performed differential scanning calorimetry measurements, optical metallography, and data analysis; MAW prepared the samples and performed optical metallography experiments; all authors contributed to the development of the experiments and description of the data.

COMPETING FINANCIAL INTERESTS

The authors declare that they have no competing financial interests.

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- [1] Ellinger, F. H., Land, C. C. & Struebing, V. O. The plutonium-gallium system. *J. Nucl. Mater.* **12**, 226-236 (1964).
 - [2] Chebotarev, N. T., Smotriskaya, E. S., Andrianov, M. A. & Kostyuk, O. E. in *Plutonium 1975 and other actinides* (ed. Blank, H. & Lindner, R.) 37 (North Holland, Amsterdam, 1976).
 - [3] Hecker, S. S. Plutonium and its alloys. *Los Alamos Sci.* **26**, 291-335 (2000).
 - [4] Hecker, S. S. & Timofeeva, L. F. A tale of two diagrams. *Los Alamos Sci.* **26**, 244-251 (2000).
 - [5] Timofeeva, L. F. in *Aging studies and lifetime extension of materials* (ed. Mallinson, L. G.) 191 (Kluwer Academic/Plenum Press, New York, 2001).
 - [6] Savrasov, S. Y., Kotliar, G. & Abrahams, E. Correlated electrons in δ -plutonium within a dynamical mean-field picture. *Nature* **410**, 793 (2001).
 - [7] Kotliar, G., Savrasov, S. Y., Haule, K., Oudovenko, V. S., Parcollet, O. & Marianetti, C. A. Electronic structure calculations with dynamical mean-field theory. *Rev. Mod. Phys.* **78**, 865 (2006).
 - [8] Shick, A., Kolorenč, J., Havela, L., Drchal, V. & Gouder, T. Multiplet effects in the electronic structure of δ -Pu, Am, and their compounds. *Euro. Phys. Lett.* **77**, 17003 (2007).
 - [9] Shim, J. H., Haule, K. & Kotliar, G. Fluctuating valence in a correlated solid and the anomalous properties of δ -plutonium. *Nature* **446**, 513 (2007).
 - [10] Marianetti, C. A., Haule, K., Kotliar, G. & Fluss, M. J. Electronic coherence in δ -Pu: A dynamical mean-field theory study. *Phys. Rev. Lett.* **101**, 056403 (2008).
 - [11] Moore, K. T. & van der Laan, G. Nature of $5f$ states in actinide metals. *Rev. Mod. Phys.* **81**, 235 (2009).
 - [12] Lashley, J. C., Singleton, J., Migliori, A., Betts, J. B., Fisher, R. A., Smith, J. L. & McQueeney, R. J. Experimental electronic heat capacities of α - and δ -plutonium: Heavy-fermion physics in an element. *Phys. Rev. Lett.* **91**, 205901 (2003).
 - [13] McCall, S. K., Fluss, M. J., Chung, B. W., McElfresh, M. W., Jackson, D. D. & Chapline, G. F. Emergent magnetic moments produced by self-damage in plutonium. *Proc. Nat. Acad. Sci.* **103**, 17179 (2006).
 - [14] Manley, M. E., Said, A. H., Fluss, M. J., Wall, M., Lashley, J. C., Alatas, A., Moore, K. T. & Shvyd'ko, Yu. Phonon density of states of α - and δ -plutonium by inelastic x-ray scattering. *Phys. Rev. B* **79**, 052301 (2009).
 - [15] Timofeeva, L. F. Phase Transformations and some laws obeyed by nonvariant reactions in binary plutonium systems. *Met. Sci. Heat Treat.* **46**, 490-496 (2004).
 - [16] Massalski, T. B. & Schwartz, A. J. Connections between the Pu-Ga phase diagram in the Pu-rich region and the low temperature phase transformations. *J. Alloy. Compd.* **444-445**, 98-103 (2007).
 - [17] Turchi, P. E. A., Kaufman, L., Zhou, S. & Liu, Z.-K. Thermostatics and kinetics of transformations in Pu-based alloys. *J. Alloy. Compd.* **444-445**, 28-35 (2007).
 - [18] Wolfer, W. G. Radiation effects in plutonium – what is known? Where should we go from here? *Los Alamos Sci.* **26**, 274-285 (2000).
 - [19] Schwartz, A. J., Wall, M. A., Zocco, T. G. & Wolfer, W. G. Characterization and modelling of helium bubbles in self-irradiated plutonium alloys. *Phil. Mag.* **85**, 479-488 (2005).
 - [20] Kubota A., Wolfer, W. G., Valone, S. M. & Baskes, M. I. Collision cascades in pure δ -plutonium. *J. Comput.-Aided Mater. Des.* **14**, 367-378 (2007).
 - [21] Hecker, S. S. Plutonium—an element never at equilibrium. *Metall. Mater. Trans. A* **39A**, 1585-1592 (2008).
 - [22] Hecker, S. S., Harbur, D. R. & Zocco, T. G. Phase stability and phase transformations in Pu-Ga alloys. *Prog. Mater. Sci.* **49**, 429-485 (2004).
 - [23] Schwartz, A. J., Cynn, H., Blobaum, K. J. M., Wall, M. A., Moore, K. T., Evans, W. J., Farber, D. L., Jeffries, J. R. & Massalski, T. B. Atomic structure and phase transformations in Pu alloys. *Prog. Mater. Sci.*, in press (2009).
 - [24] Orme, J. T., Faiers, M. E. & Ward, B. J. in *Plutonium 1975 and other actinides* (ed. Blank, H. & Lindner, R.) 761 (North Holland, Amsterdam, 1976).
 - [25] Oudot, B., Blobaum, K. J. M., Wall, M. A. & Schwartz, A. J. Supporting evidence for double-C curve kinetics in the isothermal $\delta \rightarrow \alpha'$ phase transformation in a Pu-Ga alloy. *J. Alloy. Compd.* **444-445**, 230-235 (2007).
 - [26] Imai, Y., Izumiyama, M. & Sasaki, K. Isothermal martensitic transformation in Fe-Ni-Cr alloy. *Sci. Rep.*

- RITU, A **18**, 39-48 (1966).
- [27] Rehtien, J. J. & Nelson, R. D. Phase transformations in uranium, plutonium, and neptunium. Metall. Trans. **4**, 2755-2765 (1973).
 - [28] Blobaum, K. J. M., Krenn, C. R., Wall, M. A., Massalski, T. B. & Schwartz, A. J. Nucleation and growth of the α' martensitic phase in Pu-Ga alloys. Acta Mater. **54**, 4001-4011 (2006).
 - [29] The spatial resolution of the optical metallography images is insufficient to rule out the presence of α' particles smaller than approximately $3 \mu\text{m}^2$; transmission electron microscopy micrographs would be needed to confirm the lack of particles below that threshold.
 - [30] Jeffries, J. R., Blobaum, K. J. M., Wall, M. A. & Schwartz, A. J. Microstructural evidence for conditioning-dependent $\delta \rightarrow \alpha'$ transformations in retained δ phase Pu-Ga. Acta Mater. **57**, 1831-1842 (2009).
 - [31] Cahn, J. W. On spinodal decomposition. Acta Metall. **9**, 795 (1961).
 - [32] Turchi, P. E. A., Kaufman, L., Liu, Z. -K. & Zhou, S. Thermodynamics and kinetics of phase transformations in plutonium alloys -part I. LLNL Report (2004).
 - [33] The decay of the measured heat of reversion, ΔH_R , was fit with a simple exponential function: $\Delta H_R(t) = \Delta H_R(0)\exp(-t/t_{1/2})$, where $\Delta H_R(0)$ is the heat of reversion for zero post-conditioning (*i.e.*, an optimally conditioned sample), t is the post-conditioning time, and $t_{1/2}$ is the “half-life” of the NEN.
 - [34] Jeffries, J. R., Blobaum, K. J. M., Wall, M. A., & Schwartz, A. J. Reproducible phase transformation in a single Pu-1.9 at.% Ga specimen. J. Nucl. Mater. **384**, 222-225 (2009).